Thermal properties of manganese(II) dihydrophosphate tetrahydrate

N. M. Antraptseva, T. S. Petrichenko
National University of Life and Environmental Sciences of Ukraine, Kiev, Ukraine,
e-mail: aspirant_nubipu@ukr.net

Heat treatment of crystal hydrates is one of the ways to obtain anhydrous salts. This process in many respects is defined by an extent of hydration of crystalline hydrate. The thermal transformation of manganese(II) dihydrophosphate dihydrate $Mn(H_2PO_4)_2 \cdot 2H_2O$ have been determined [1]. Thermal properties of $Mn(H_2PO_4)_2 \cdot 4H_2O$ tetrahydrate are studied insufficiently. The aim of this work was to study thermal behaviour of $Mn(H_2PO_4)_2 \cdot 4H_2O$ to determine the sequence of thermal and structural transformations and how the extent of hydration affects these transformations.

Thermal transformations were studied, as in [1], using Q-1500D derivatograph. According to the results of the differential and thermal analysis, $Mn(H_2PO_4)_2 \cdot 4H_2O$ is resistant when heating in air with a rate of 2.5 K/min to 50 °C. Further temperature increase is followed by a loss of weight. It is registered by four accurate steps on TG curve.

Interpreting the results of the complex characterization of the products of partial and complete dehydration of $Mn(H_2PO_4)_2 \cdot 4H_2O$, we found the following. Heat treatment of $Mn(H_2PO_4)_2 \cdot 4H_2O$ in the range of 50–110 °C is followed by the removal of two molecules of water by the molecular mechanism and the formation of $Mn(H_2PO_4)_2 \cdot 2H_2O$. At the same time partly the process of the anion disproportionation is realized with the formation of $MnHPO_4 \cdot 3H_2O$ and H_3PO_4.

The second stage of dehydration ends up in the range of 110–160 °C with the formation of two mixed crystalline phases which are $Mn(H_2PO_4)_2$ and $Mn_5(HPO_4)_2(PO_4)_2 \cdot 4H_2O$. The quantity of free H_3PO_4 in the thermolysis products of $Mn(H_2PO_4)_2 \cdot 4H_2O$ increases and at 160 °C it makes 2.12 wt % (based on P_2O_5).

The process of the anion condensation begins at the third stage of $Mn(H_2PO_4)_2 \cdot 4H_2O$ thermolysis. At 185 °C the losses of the weight correspond to a removal of 4.55 mol of H_2O. The salt component includes the condensed phosphate with n = 2–5. The acid component includes polyphosphoric acids of the general formula $H_{n+2}P_nO_{3n+1}$ (n = 2–4).

Most difficult it is to determine the composition of the products at heating of $Mn(H_2PO_4)_2 \cdot 4H_2O$ to 275 °C. It is presented by a mixture of condensed phosphates and polyphosphoric acids with $2 \leq n \leq 7$. The condensed phosphates with n = 3–8 are X-ray amorphous.

At heating of $Mn(H_2PO_4)_2 \cdot 4H_2O$ to 300 °C the anion composition of thermolysis products is simplified. The finish products of dehydration appear. It is identified as cyclotetraphosphate with composition of $Mn_2P_4O_{12}$. Its crystallization ends up at 335°C.

Thus, the sequence of thermal solid-phase transformations accompanying $Mn(H_2PO_4)_2 \cdot 4H_2O$ thermolysis was established. The composition of the products of its partial and full dehydration was identified; the temperature intervals of their formation and thermal stability were concretized. It was shown that the final product of thermolysis is $Mn_2P_4O_{12}$ (monoclinic system, sp. gr. *C2/c, Z = 4*; a = 1.2084, b = 0.8471, c = 1.0171 nm; β = 119.29°) is formed by two directions. The first direction provides thermal dehydration of the protonated condensed phosphates (up to 65 %). According to the second direction, up to 35 % of $Mn_2P_4O_{12}$ is formed as a result of solid-phase interactions of thermolysis intermediate products. The general scheme of thermal solid-phase transformations of $Mn(H_2PO_4)_2 \cdot 4H_2O$ was proposed.

References

1. L.N. Shchegrov, N.M. Antraptseva, I.G. Ponomareva. Izv. Akad. Nauk SSSR, Neorg. Mater. (1989) 25 (2): 308.